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# Design of ordered microstructures of block copolymers

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ブロック共重合体がつくるマイクロ相分離構造にたいして、「ある相分離構造を得るためには、どのような高分子鎖を用いればよいか」という問題に取り組んだ。この問題の解決手法と簡単なデモンストレーションを示す。

Block copolymer melts have been received much attention for their ability to self-assemble into various ordered structures. These ordered structures are called microphase-separated structures. Formation of these structures are strongly affected by the monomer sequence along the polymer chain and the various interactions between different types of monomers.

This phenomenon of microdomain formation has been studied by the self consistent field theory[1] and the density functional theory[2] in which the free energy is represented by a functional of the densities of each types of monomers. Although these theories are quite successful, they do not answer the question "How to generate the desired microphase separated structure?"

In this work, we propose a method to answer this question. Figure 1 is a schematic picture showing a comparison between our strategy and existing ones. In the existing works, the configuration(monomer sequence) is fixed while various phase-separated structures are scanned to look for the equilibrium structure that minimizes the free energy. By contrast, in our proposed method, the phase-separated structure is fixed to the desired one, and the chain configuration is scanned. In this way, we can find the copolymer which gives the lowest free energy at the desired microphase-separated structure.

As an example, we consider melts of gradient copolymers[3]. To characterize the configuration of the gradient copolymers, we introduce a monomer distribution function  $K(s)$ , which is the probability of finding a monomer of the type  $K$  at the  $s$ -th monomer. We expand this monomer distribution function  $K(s)$  in Fourier series and use the Fourier coefficients  $\{K_p\}$  to specify the chain configuration. Using this description of the configuration of the polymer, we can calculate the density correlation functions by the standard procedure of the random phase approximation. These density correlation functions are used as the expansion coefficients of the free energy. As the density correlation functions depend on the set of Fourier coefficients  $\{K_p\}$ , the free energy can be written in terms of  $\{K_p\}$ . The condition that a polymer configuration

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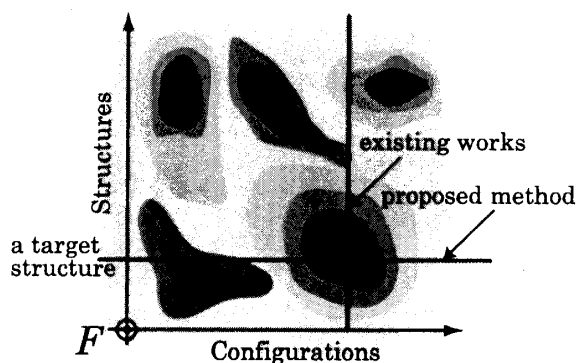


Figure 1: A schematic picture of the proposed method. In the existing works, the configuration is fixed while the structures are changed. In our work, the structure is fixed at the desired one while the configurations are changed.

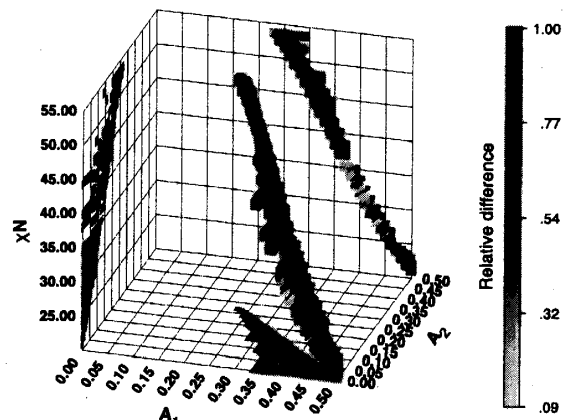


Figure 2: The suitable polymers to an asymmetric lamellar structure that has two different widths of the interfaces. In this parameter space, the most suitable polymer is  $A_1 = 0.4$ ,  $A_2 = 0.05$ ,  $\chi N = 30.0$ .

minimizes the free energy does not guarantee that the polymer actually assembles into the target microphase separated structure, because there may be more stable phase-separated structures than the target one. Here we adopt an assumption that the desired phase-separated structure might be a thermodynamic meta-stable structure. The condition of the thermodynamic meta-stability can be judged using the first and second derivatives of the free energy.

For a demonstration, we assume that the desired structure is an asymmetric lamellar structure of an A-B type diblock copolymer that has two interface widths. The result is shown in Figure 2. Three axes of the graph are the Fourier coefficients  $A_1$  and  $A_2$ , and the A-B interaction parameter multiplied by the chain length  $\chi N$ , respectively. Plotted are the points where the free energy is lower than that of the uniform disordered state and has a local minimum (stable or meta-stable). The gray scale chart shows the relative difference in the monomer density profile between the desired structure and the thermodynamically stable structure. This graph shows that the most desirable polymer corresponds to a diblock-like copolymer with a smooth transition region.

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